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(54) **Alkylation of polycyclic aromatic compounds to alkylates enriched in the para-substituted isomers**

Alkylierung von polzyklischen aromatischen Verbindungen unter Bildung von mit den para-substituierten Isomeren angereicherten Alkylaten

Alcoylation de composés polycycliques aromatiques avec formation d'alcoylates enrichis d'isomères parasubstitués

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Description

This invention relates to mordenite zeolites and their use as catalysts in the alkylation of aromatic compounds to alkylates enriched in the para-substituted isomers.

5 The para,para'-dialkylates (p,p'-dialkylates) of aromatic hydrocarbons, such as 4,4'-dialkylated biphenyl or 2,6'-dialkylated naphthalene, are valuable intermediates in the preparation of monomers from which thermotropic liquid crystal polymers are synthesized. Liquid crystal polymers are high molecular weight polymers which naturally exist in or can form liquid-crystal states. The liquid-crystal state is a highly anisotropic fluid state which possesses some properties of a solid and some properties of a conventional, isotropic liquid. For example, the typical liquid crystal flows like a fluid, while retaining much of the solid state molecular order. Thermotropic liquid crystals refer to those liquid crystals which are formed by the adjustment of temperature. Generally, for a molecule to possess a liquid-crystal state the molecule must be elongated and narrow, and the forces of attraction between these molecules must be strong enough for an ordered, parallel arrangement to be maintained after melting of the solid. Thus, bulky substituents positioned anywhere but on the ends of an elongated molecule will usually destroy the liquid-crystal state. Accordingly, p,p'-disubstituted aromatic compounds are likely to exhibit liquid crystal-line properties, whereas meta- and ortho-disubstituted aromatic compounds are not. Thermotropic, liquid crystal polymers find utility in the formation of ultra high-strength fibers and films. An overview of liquid crystals may be found in Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Volume 14, John Wiley & Sons, New York, N.Y., pp. 395-427.

20 One group of monomers from which thermotropic liquid-crystal polymers are synthesized is the p,p'-dihydroxy poly-nuclear aromatics. Phenol, for example, is dialkylated at the ortho positions with isobutylene, and the resulting dialkylated phenol is coupled at the para position to form 3,3',5,5'-tetra(i-butyl)-4,4'-dihydroxybiphenyl. (See U.S. Patent 4,108,908.) This substituted biphenyl is dealkylated to yield p,p'-dihydroxybiphenyl, which reacts with aromatic diacids and hydroxy acids to form liquid crystal polymers. Aromatic diacids are also prepared in a multi-step process. p-Chlorotoluene, for example, is coupled to form 4,4'-dimethylbiphenyl, which is subsequently oxidized to 4,4'-biphenyldicarboxylic acid. (See U.S. Patent 4,263,466.)

25 As illustrated in the examples hereinbefore, the syntheses of dihydroxy polynuclear aromatics and diacids require considerable effort. An alternate route based on the direct alkylation of polynuclear aromatics would require fewer starting materials and fewer steps. For example, if biphenyl could be dialkylated with propylene selectively to p,p'-(diisopropyl)biphenyl, the latter could be converted directly to p,p'-dihydroxybiphenyl or to p,p'-biphenyldicarboxylic acid. Thus, 30 the selective alkylation of polynuclear aromatic compounds would greatly simplify the syntheses of dihydroxyl polynuclear aromatics, diacids and hydroxy acids which are the building blocks for liquid crystal polymers.

35 It is known that aromatic hydrocarbons can be alkylated in the presence of acid-treated zeolite U.S. Patent 3,140,253 (1964) and U.S. Patent 3,367,884 (1968) broadly teach the use of acid-treated mordenite for the alkylation of aromatic compounds. However, such alkylations are generally not selective with respect to site and number of substitutions.

More specifically, some of the prior art illustrates the use of acid-treated zeolites in the alkylation of polycyclic aromatic compounds. For example, U.S. Patent 3,251,897 teaches the alkylation of naphthalene by acid-treated zeolites X, Y, and mordenite. However, the conversion of naphthalene is shown to be low, and the selectivity to di- and triisopropyl naphthalenes is low and otherwise unspecified. Japanese Patent 56-156,222 (1981) teaches the alkylation of biphenyl using silica alumina catalysts to give the monalkylate in a para/meta ration of 3/2. U.S. Patent 4,480,142 (1984) discloses the alkylation of biphenyl in the presence of an acid-treated montmorillonite clay to yield 2-alkylbiphenyls as the major product.

40 Some of the prior art describes the use of acid-treated zeolites for the preparation of dialkylates high in para isomer content. For example, Japanese Patents 56-133,224 (1981) and 58-159,427 (1983) teach the use of acid extracted mordenite for the gas phase alkylation of benzene or monoalkylbenzenes to p-dialkylbenzenes. U.S. Patent 4,283,573 (1981) discloses the alkylation of phenols by use of H-mordenites to produce p-alkyl phenols with placement of the phenolic moiety at the 2-position of the alkyl chain. U.S. Patent 4,361,713 (1982) describes the treatment of numerous ZSM zeolite catalysts with a halogen-containing molecule, such as HCl, or CCl_4 , and calcination at a temperature of from 300°C to 600°C to enhance the para-selective properties of such catalysts in the alkylation of benzene compounds. As 45 illustrated with toluene, the conversion is taught to be low, while the selectivity to p-xylene is taught to be high.

Most recently, European Patent Application 0-202,752 (1986) teaches the alkylation of multi-ring aromatic hydrocarbons to alkylated derivatives high in β and β,β' isomers. The process involves contacting a multi-ring aromatic hydrocarbon with an alkylating agent other than an alcohol, such as an alkylaromatic hydrocarbon, in the presence of a medium- or large-pore, acid-treated zeolite.

50 EP-A2-0,029,333 discloses a catalytic method for producing alkyl-substituted phenolic compounds with preferential production of para-alkylphenols. The catalyst is a crystalline zeolite having a network of pores with openings having a major dimension from 6 to 7 Angstrom (0.6 to 0.7 nm). The reference teaches dealuminizing the zeolite by treating it with 0.5N hydrochloric acid under reflux conditions but does not teach the selection of a starting mordenite by a particular Symmetry Index.

In GB-A-1,334,928, a catalytic composition is described which comprises a crystalline aluminosilicate of the mordenite type having a silica to alumina mole ratio of at least 40:1 and being prepared by extracting aluminum with a mineral acid of at least 1N concentration from an initial mordenite composition having a silica to alumina molar ratio of from 12:1 to 30:1. The catalyst is useful for alkylating alkylatable hydrocarbons using an olefin as alkylating agent. There is 5 no mention of calcining or heating an acidic mordenite prior to the said extracting step.

GB-A-1,261,616 is concerned with the production of a crystalline zeolite having a reduced alumina content. In the process, a mordenite is calcined in the hydrogen exchanged (i.e. acidic) form and thereafter leached with an acid to reduce the alumina content. The reference is silent with respect to the Symmetry Index of the starting mordenite and the mordenite after calcination and leaching.

10 Despite the numerous teachings in the prior art, there are few useful results of the alkylation of aromatic compounds particularly polycyclic aromatic compounds, by zeolite catalysts. Such alkylations tend to give low conversion of the aromatic compound, and a low yield of the desirable p,p'-dialkylates or linear alkylates. A variety of by-products of low value is produced, making the separation and isolation of products difficult, if not impractical.

15 It would be highly desirable to find a process for the alkylation of aromatic compounds which would give high yields of disubstituted aromatic compounds enriched in the para alkylated isomers. Such a process would therefore find widespread utility in the synthesis of monomers for the preparation of thermotropic liquid crystal polymers.

20 In one aspect, this invention is a process of alkylating an aromatic compound to a mixture of substituted aromatic compounds enriched in the para or linear alkylated isomers, comprising the steps of contacting the aromatic compound with an alkylating agent in the presence of a catalyst and at a temperature in the range from 100°C to 400°C and under a pressure in the range from 170kP to 3549kP (10 to 500psig), said catalyst comprising an acidic mordenite zeolite having a silica/alumina molar ratio of at least 50:1 and a crystalline structure which is determined by X-ray diffraction to possess a Symmetry Index of at least 1.0, said catalyst being prepared by a process which comprises:

25 (A) calcining in air or heating in an inert atmosphere an acidic mordenite zeolite having a Symmetry Index between 0.50 to 1.0 and a silica/alumina molar ratio less than 40:1, and thereafter
 (B) contacting the calcined or heated acidic mordenite zeolite with a strong acid to remove an amount of alumina sufficient to provide a silica/alumina ratio of at least 50:1, and optionally
 (C) repeating at least once the steps of (A) calcining or heating and (B) contacting with strong acid to remove additional alumina.

30 One embodiment of the above process is a process of alkylating biphenyl to a mixture of disubstituted products enriched in 4,4'-dialkyl-1,1'-biphenyl. Another embodiment is a process of alkylating benzene to a mixture of disubstituted products enriched in p-dialkylated benzene. In both of the said embodiments the process parameters are as described for the above process.

35 Surprisingly, under the conditions of this process the conversion of the aromatic compound is higher than the conversions known heretofore. Moreover, under the conditions of this process the selectivity to the corresponding para alkylated isomers is higher than known heretofore. Consequently, the yield of para alkylated aromatic products is significantly higher than the yield of such products obtained by the alkylations disclosed in the prior art.

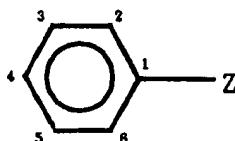
40 The para alkylated aromatic compounds prepared by the process of this invention are useful intermediates in the preparation of monomers for thermotropic, liquid crystal polymers.

In another aspect, this invention is a novel catalyst composition comprising an acidic mordenite zeolite having a silica/alumina molar ratio of at least 50:1, a Symmetry Index of at least about 1, and a porosity such that the total pore volume is in the range of from 0.18cm³/g to 0.45cm³/g, and the ratio of the combined meso- and macropore volume to the total pore volume is from 0.25 to 0.75, said catalyst being prepared by a process which comprises:

45 (A) calcining in air or heating in an inert atmosphere an acidic mordenite zeolite having a Symmetry Index between 0.50 to 1.0 and a silica/alumina molar ratio less than 40:1, and thereafter
 (B) contacting the calcined or heated acidic mordenite zeolite with a strong acid to remove an amount of alumina sufficient to provide a silica/alumina ratio of at least 50:1, and optionally
 50 (C) repeating at least once the steps of (A) calcining or heating and (B) contacting with strong acid to remove additional alumina. For the purposes of this invention, a micropore has a radius in the range of from 3 angstrom units (Å) to 10 Å, a mesopore has a radius in the range of from 10 Å to 100 Å, and a macropore has a radius in the range of from 100 Å to 1000 Å.

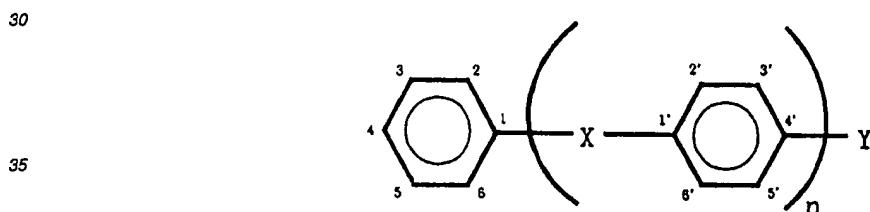
55 In a further aspect, this invention is a process of preparing the catalyst composition identified herein-above comprising the steps of (A) first calcining or heating and then (B) contacting with a strong acid an acidic mordenite zeolite having a silica/alumina molar ratio of less than 40:1 and a crystalline structure determined by X-ray diffraction to possess a Symmetry Index of from 0.5 to 1.0 under conditions sufficient to remove an amount of alumina to provide a silica/alumina ratio of at least 50:1.

The aromatic compound which is employed in the process of this invention is any monocyclic or polycyclic aromatic compound. Any monocyclic aromatic compound is suitable provided that at least one of the para positions is unsubstituted. Such suitable compounds include benzene; linear and branched alkylbenzenes, such as toluene, ethylbenzene, n-propylbenzene, cumene, butylbenzenes including t-butylbenzene, phenylcyclohexane, o- and m-xlyenes, and mesitylene; alkoxy-substituted benzenes, such as anisole and phenetole; polyalkylene oxide-substituted benzenes, such as polyethylene oxide phenyl ether, or polypropylene oxide phenyl ether; thiophenol and phenylalkyl thiols; halogenated benzenes, such as fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, and their o- and m-dihalogenated homologues; and phenyl sulfides, such as methyl phenyl sulfide, or ethyl phenyl sulfide. Preferably, the monocyclic aromatic compound is unsubstituted, or substituted with no more than one substituent. More preferably, the monocyclic aromatic compound is represented by the formula:



20 wherein Z is hydrogen, sulphydryl, alkyl of C₁-10 carbon atoms, aliphatic alkoxy or thioalkoxy of C₁-10 carbon atoms, fluoro, chloro, or bromo. Even more preferably, the monocyclic aromatic compound is benzene, cumene, t-butylbenzene, or anisole. Most preferably, the monocyclic aromatic compound is benzene or cumene.

The polycyclic aromatic compound of the invention is any aromatic compound containing a plurality of aromatic rings. The aromatic rings may be fused, like naphthalene, or non-fused ring assemblies, like biphenyl. The nomenclature and numbering of the fused and non-fused polycyclic compounds of this invention follow standard practice as found in *Nomenclature of Organic Chemistry*, International Union of Pure and Applied Chemistry, Butterworths, London, 1969, pp. 20-31 and 42-46. If fused, the aromatic compound preferably contains up to three rings. If non-fused, the polycyclic aromatic compound is represented by the preferred formula:



40 wherein n is a positive number from 1 to 3; Y is hydrogen, hydroxyl, sulphydryl, alkyl of C₁-10 carbon atoms, aliphatic alkoxy or thioalkoxy of C₁-10 carbon atoms, fluoro, chloro or bromo; and X may be absent or present. If absent, the phenyl rings are bonded at the 1,1' positions to each other. If present, X may be O, S, SO, SO₂, CH₂, CH₂CH₂, CH₂CH₂CH₂ or CHCH₃. In addition to being fused or non-fused, the aromatic rings may also be substituted or unsubstituted. If substituted, the substituents may be at any position providing that at least one of the para (non-fused) or beta (fused) positions is unsubstituted. If the polycyclic aromatic compound is biphenyl, for example, the ortho (2,6) and meta (3,5) positions and one of the para (4) positions may be substituted. If the polycyclic aromatic hydrocarbon is naphthalene, the alpha (1,4,5,8) and beta (2,3,6,7) positions may be substituted, providing at least one beta position remains unsubstituted. The substituent may be a C₁-C₂ alkyl moiety, such as methyl or ethyl; fluoro; chloro; hydroxyl; or a C₁-C₂ alkoxy. However, if the substituent is "Y" as shown in the preferred formula, the substituent may include larger moieties as described hereinbefore. Preferably, the polycyclic aromatic compound is unsubstituted, or substituted with no greater than one C₂ moiety. More preferably, the polycyclic aromatic compound is unsubstituted. Examples of suitable polycyclic aromatic compounds which may be used in the invention are biphenyl, diphenyl ether, 4-hydroxy-1,1'-biphenyl, 4-phenoxy-1,1'-biphenyl, diphenylsulfide, terphenyl, tetraphenyl, diphenylmethane, 1,2-diphenylethane, 1,3-diphenylpropane, methylbiphenyls, ethylbiphenyls, 3- or 4-isopropylbiphenyl, naphthalene, methylnaphthalenes, ethynaphthalenes, beta-isopropynaphthalenes, and the like. Preferably, the polycyclic aromatic compound is a C₁₀-C₂₄ compound. More preferably, the polycyclic aromatic compound is an unsubstituted, fused or non-fused C₁₀-C₂₄ compound. Most preferably, the polycyclic aromatic hydrocarbon is biphenyl, diphenyl ether, or naphthalene.

The aromatic compound may be used neat in a liquid state, or dissolved in a suitable solvent. Preferably, the aromatic compound is used in a neat liquid state. If a solvent is employed, any inert solvent which solubilizes the aromatic

compound and does not hinder the alkylation reaction may be used. The preferred solvent is 1,3,5-triisopropylbenzene or decalin.

The alkylating agent suitable for alkylating the above-identified aromatic compounds may be selected from a variety of materials, including monoolefins, diolefins, polyolefins, alcohols, alkyl halides, alkylsulfates, alkylphosphates, dialkylethers, and alkylaromatics. Exemplary of the monoolefins which may be employed in the process are ethylene, propylene, n-butene, isobutylene, 1-pentene, 1-hexene, cyclohexene, and 1-octene. 1,3-Butadiene is an example of a suitable diolefin. Alcohols, such as methanol, ethanol, isopropyl alcohol, isobutyl alcohol, pentyl alcohol, hexanol, and iso-hexanol, and alkyl halides, such as methyl chloride, isopropyl chloride, ethyl bromide, and methyl iodide are also suitable for use in the process. Alkylaromatics, such as xylenes, trimethylbenzenes, and the like, make suitable alkylating agents, as do ethers, such as dimethylether, diethylether, ethylpropylether, and diisopropylether. The preferred alkylating agent is a monoolefin, a diolefin or an alcohol. The more preferred alkylating agent is a monoolefin selected from the group consisting of propylene, n-butene, 1-hexene, cyclohexene, and 1-octene. Most preferably, the alkylating agent is propylene or n-butene.

The catalyst of the invention is an acid-modified zeolite with interconnecting twelve-ring and eight-ring channels. Zeolites have framework structures that are formally constructed from silicate and aluminate tetrahedra that share vertices. The tetrahedra may be linked to form pores or channels. The size of the pores is determined by the number of tetrahedra in the ring. Twelve-ring zeolites contain rings formed from twelve tetrahedra. Eight-ring zeolites contain rings formed from eight tetrahedra. The zeolites of this invention contain interconnecting twelve-ring and eight-ring channels. Examples of the zeolites suitable for use in this invention are mordenite, offretite and gmelinite. Mordenite-like zeolites, such as ECR-1, described in U. S. Patent No. 4,657,748, issued April 14, 1987, and intergrowths of mordenite with other zeolites are also suitable catalysts; as are zeolites having a one-dimensional pore system with twelve-ring channels, such as type L or related zeolites. Preferably the catalyst is an acidic mordenite zeolite.

Mordenite is an aluminosilicate whose typical unit cell contents are assigned the formula $\text{Na}_8[(\text{AlO}_2)_8(\text{SiO}_2)_{40} \cdot 24 \text{H}_2\text{O}]$. Mordenite is the most siliceous natural zeolite with a silicon/aluminum mole ratio (Si/Al) of about 5/1. The dimensions of the twelve-ring pores are about $6.7 \times 7.0 \text{ \AA}$; the dimensions of the eight-ring pores are about $2.9 \times 5.7 \text{ \AA}$. The structure and properties of mordenite zeolite are described in Zeolite Molecular Sieves, by Donald W. Breck (John Wiley & Sons, 1974), at pages 122-124 and 162-163.

The catalyst of this invention is prepared from a mordenite zeolite typically containing cations of the alkali or alkaline earth metals, or alternatively ammonium ions. Preferably, the catalyst of the invention is prepared from a sodium mordenite zeolite; even more preferably, from a sodium mordenite zeolite having a Symmetry Index less than about 1.0. The Symmetry Index is a dimensionless number obtained from the X-ray diffraction pattern of the sodium mordenite being measured in the hydrated form. Standard techniques are employed to obtain the X-ray data. The radiation is the K_{α_1} line of copper, and a Philips Electronics spectrometer is used. The mordenite zeolites exhibit an X-ray diffraction pattern whose diffraction peaks have d-spacings corresponding to those of crystalline mordenites as reported by J. D. Sherman and J. M. Bennett in "Framework Structures Related to the Zeolite Mordenite," Molecular Sieves, J.W. Meier and J.B. Uytterhoeven, eds., Advances in Chemistry Series, 121, 1973, pp. 52-65. The Symmetry Index is defined as the sum of the peak heights of the [111] (13.45, 2 θ) and [241] (23.17 2 θ) reflections divided by the peak height of the [350] (26.25 2 θ) reflection. Preferably, the Symmetry Index of the sodium mordenite ranges from 0.50 to 1.0. More preferably, the Symmetry Index of the sodium mordenite ranges from 0.60 to 1.0.

Four ordered crystalline structures have been proposed to describe the X-ray diffraction data available for natural and synthetic mordenite zeolites. (J. D. Sherman and J. M. Bennett, *op.cit.*, p. 53.) The symmetries of these four structures are Cmcm, Cmmm, Imcm, and Immm as these terms are defined by N. F. M. Henry and K. Lonsdale in International Tables for X-ray Crystallography, 3rd Ed., Volume 1, Kynoch Press (1969). X-ray diffraction data indicate that mordenites are either physical admixtures or intergrowths of the Cmmm, Imcm, or Immm structures with the Cmcm structure. Thus, mordenites can be generally described as having a crystalline structure comprising a matrix of Cmcm symmetry having dispersed therein domains of Cmmm, Imcm, or Immm symmetry, or mixtures thereof. The Symmetry Index is related to the symmetries of the crystals present in the mordenite sample. A Symmetry Index in the range from 0.60 to 1.0 provides the optimum sodium mordenite as starting material for the process of this invention.

The crystallite size of the original sodium mordenite may be any size which yields a catalyst selective for alkylated aromatic compounds enriched in the para isomers. Typically, the crystallite size may be in the range from 500 \AA to 5000 \AA , preferably from 500 \AA to 2000 \AA , more preferably from 800 \AA to 1500 \AA . Generally, the crystallites form aggregates which may be used as such or bound into larger particles for the process of this invention. For example, extrudate can be made for a packed-bed reactor by compressing the aggregates into binderless particles of suitable sizes. Alternatively, the extrudate can be made via use of binders well-known to those in the art. The preferred particle size ranges from about 1 micron (μ) to about 20 μ .

The original sodium mordenite zeolite described hereinabove, or its equivalent, is treated to obtain the catalyst of the invention for use in the alkylation process. The treatment involves contacting the mordenite with acid. Preferably, the treatment involves contacting the mordenite with acid, calcining the acid-treated mordenite, and further contacting the calcined mordenite with strong acid.

The initial acid treatment serves to remove most of the sodium ions, or their equivalents, from the original mordenite. The treatment may remove a portion of the aluminum ions as well. Inorganic acids and organic acids are suitable compounds from which the hydrogen ions are obtained for the acid treatment. Examples of such acids are hydrochloric acid, hydrobromic acid, sulfuric acid, phosphoric acid, nitric acid, acetic acid, oxalic acid, and the like. Inorganic acids

5 are the preferred source of hydrogen ions; with hydrochloric, nitric and phosphoric acids being more preferred and hydrochloric acid being most preferred. An equally acceptable initial treatment involves ion exchange with ammonium salts, such as ammonium chloride. By this method the sodium ions, or their equivalents, are removed, but the aluminum ions are not displaced. On heating the ammonium exchanged mordenite, ammonia is given off and the mordenite is converted to the acid form.

10 Typically, in the initial acid treatment the original sodium mordenite is slurried with an aqueous solution of the acid. The acid solution may have any concentration, providing the catalyst obtained possesses the properties and activity of the catalyst of this invention, these being described hereinafter. Preferably, the concentration of the aqueous acid solution is in the range from 0.01N to 6N, more preferably from 0.5N to 3.0N. The relative quantities of aqueous acid solution to mordenite solid which are employed may vary. Typically, the ratio is less than about 15 cc acid solution per gram mordenite solid. Preferably, the ratio is in the range from 5 cc to 10 cc acid solution per gram mordenite solid. The temperature and the duration of the contact of the mordenite with the acid solution may also vary. Preferably, the mordenite is contacted with the acid at a temperature in the range from 10°C to 100°C. Generally, the contact time between the acid solution and the mordenite may vary from 5 minutes to several hours. It is important that there be sufficient time for the acid solution to contact all of the mordenite particles. Preferably, the contact time is from 5 minutes to 60 minutes. The 15 acid extraction, as described herein, may be repeated if desired. Afterwards, the mordenite is washed in water one or more times in order to rinse away soluble species from the mordenite. Preferably, the water wash is carried out at ambient temperature. Optionally, subsequent to the water wash the mordenite is dried in air at a temperature in the range from 20°C to 150°C.

20 Following the exchange with acid and drying in air, the acidic mordenite zeolite is calcined in air or heated in an inert atmosphere, such as nitrogen. It is believed that this heat treatment dislocates a portion of the aluminum from the zeolite framework; however, such a theory should not be taken as limiting of the scope of the invention. Typically, the temperature of the calcination or heating may range from 250°C to 950°C, preferably from 300°C to 800°C, more preferably from 400°C to 750°C, and most preferably from 500°C to 700°C.

25 After calcining or heating the acid-treated mordenite described hereinabove, the mordenite is subjected to an additional acid treatment for the purpose of further dealumination. The second acid treatment comprises contacting the calcined or heated mordenite with a strong acid under conditions sufficient to produce the acidic mordenite catalyst of this invention. For the purposes of this invention a "strong" acid is defined as an acid which reacts essentially completely with the solvent to give the conjugate acid of the solvent. For example, if gaseous hydrogen chloride is dissolved in water, the acid-base reaction is complete to give the conjugate acid H_3O^+ and Cl^- . Preferably, the strong acid is an inorganic acid. More preferably, the strong acid is nitric acid, hydrochloric acid, or sulfuric acid. Most preferably, the strong acid is nitric acid. The concentration of the strong acid will vary depending on the acid selected. In general, the acid is employed in an aqueous solution of any concentration which provides for the extraction of aluminum from the calcined acidic mordenite, as described hereinafter. With nitric acid, for example, the concentration of the acid in the aqueous solution is preferably in the range from 2N to 15N, more preferably from 4N to 12N, and most preferably from 6N to 8N. 30 The aqueous acid solution and the calcined or heated mordenite are contacted in any ratio that provides the catalyst of the invention. Preferably, the ratio of aqueous acid solution to mordenite is in the range from 3 to 10 cc acid solution per gram mordenite, more preferably the ratio is about 5 cc acid solution per gram mordenite. The temperature and the duration of the contact may vary depending on the acid selected. Preferably, the mordenite is contacted with the acid solution at a temperature in the range from ambient temperature, taken as 22°C, to 220°C, more preferably at a temperature which allows for boiling of the aqueous acid under atmospheric conditions. Preferably, the duration of the contact is from 1 to 6 hours, more preferably from 1 to 3 hours, most preferably for about 2 hours. When the contacting with strong acid is complete, the mordenite is filtered and washed repeatedly with water until the washings are acid-free. Preferably, the washed mordenite is heat treated and contacted with strong acid more than once. Lastly, the washed acidic mordenite zeolite is dried for several hours at a temperature in the range from 100°C to 150°C to remove physically adsorbed water. The dried acidic mordenite is activated by heating for about 2 hours at a temperature of from 300°C to 700°C. This activation may drive off more strongly bound water and any residual adsorbates.

35 After the original sodium mordenite is treated with acid, calcined, and retreated with strong acid according to the process of this invention, an acidic mordenite catalyst is obtained which is capable of converting an aromatic compound in a high conversion to a mixture of substituted aromatic compounds enriched in the para or linear alkylated isomers. 40 This catalyst exhibits special characteristics by which it may be identified, specifically, the silica/alumina molar ratio, and the Symmetry Index and porosity as defined hereinafter.

45 As a result of the acid extractions, the silica/alumina molar ratio (SiO_2/Al_2O_3) of the acidic mordenite catalyst is increased over that of the original sodium mordenite. Specifically, the acid-treated mordenite catalyst has a silica/alumina molar ratio of at least 50:1, preferably at least 150:1, and most preferably from 200:1 to 1000:1.

As a further result of the acid extractions and calcination, the Symmetry Index of the mordenite catalyst is increased over that of the original mordenite. The Symmetry Index is as defined hereinbefore. Since the Symmetry Index is derived from X-ray data, the Index is related to the proportion of Cmcm and Cmmm symmetries present in the catalyst. The increase in the Symmetry Index is indicative of the enrichment of the catalyst in the Cmcm component. A Symmetry Index of at least about 1.0 results in catalysts capable of achieving high yields of the para or linear alkylated polycyclic aromatic compounds. The preferred Symmetry Index ranges from 1.0 to 2.0, more preferably from 1.5 to 2.0.

A third property of the acidic mordenite catalyst, by which it is identified, is the porosity. All zeolites possess pores which form as a natural consequence of zeolite crystal growth. New pores or modifications of existing pores can occur on treating the zeolites, for example, with heat or acid as in the process of this invention. Typically, pores are classified into micropores, mesopores and macropores. For the purposes of this invention a micropore is defined as having a radius in the range from 3 Angstrom units (3 Å) to 10 Å. Likewise, a mesopore is defined as having a radius in the range from 10 Å to 100 Å, while a macropore is defined as having a radius from 100 Å to 1000 Å. After calcination or heating and strong acid treatment, the acidic mordenite catalyst of this invention possesses micro-, meso- and macropores. The porosity of the catalyst may be distinguished by the total pore volume defined as the sum of the volumes of the micro-, meso-, and macropores per gram catalyst. A catalyst of this invention has a total pore volume sufficient to provide a high yield of para alkylated isomers in the alkylation of an aromatic compound. Preferably, the total pore volume is in the range from 0.18 cc/g to 0.45 cc/g. The porosity may be further distinguished by the relative distribution of meso- and macropores, as found in the ratio of the combined meso- and macropore volume to the total pore volume. A catalyst of this invention has a ratio of combined meso- and macropore volume to total pore volume sufficient to provide a high yield of para alkylated isomers in the alkylation of an aromatic compound. Preferably, the ratio of the combined meso- and macropore volume to total pore volume is in the range from 0.25 to 0.75.

The measurement of the porosity, described hereinabove, is derived from surface area and pore volume measurements of mordenite powders obtained on any suitable instrument, such as a Quantachrome Digisorb-6 unit, using nitrogen as the adsorbate at the boiling point of nitrogen, 77 K. The total pore volume (V_T) is derived from the amount of nitrogen adsorbed at a relative pressure close to unity. It is accepted that this volume constitutes pores of less than 1000 Å in radius. Pores having a radius in the 10 Å to 1000 Å range are known in the literature as "transitional pores." The micropore volume (V_m) in the presence of "transitional pores" is obtained by the t-method. The difference between the total pore volume and the micropore volume is the transitional pore volume, ($V_t = V_T - V_m$). The cumulative pore distribution in the transitional pore range is used to calculate the relative volume contributions of mesopores and macropores. For example, the mesopore volume is calculated by multiplying the transitional pore volume by the fraction of the cumulative pore volume from 10 Å to 100 Å, ($V_{me} = V_t f_{me}$). The macropore volume is then simply obtained by subtracting the mesopore volume from the transitional volume, ($V_{ma} = V_t - V_{me}$). This approach ensures that the equation $V_T = V_m + V_{me} + V_{ma}$ is satisfied. The adsorption isotherms obtained for the mordenite catalysts of this invention are of Type I, which are described by the Langmuir equation. The Langmuir surface area is obtained from such equation. The methods used to obtain surface areas and pore volumes are described by S. Lowell in Introduction to Powder Surface Area (John Wiley and Sons, 1979), or in the manuals provided with the Digisorb-6 instrument made by the Quantachrome Corporation.

The acidic mordenite catalyst, identified hereinabove, is capable of adsorbing biphenyl into the intracrystalline pore system, and conversely desorbing biphenyl. Biphenyl adsorption is effected by exposing the acidic mordenite to biphenyl vapors at 100°C for a time sufficient to obtain near constant weight. Preferably, the adsorption capacity of the acidic mordenite for biphenyl is about 5 weight percent. More preferably, the capacity is about 10 weight percent. Biphenyl desorption is effected by heating the mordenite-biphenyl sample in a dynamic helium atmosphere from 25°C to 1000°C at a heating rate of about 10°C/minute. The desorption of biphenyl may be followed experimentally by thermal gravimetric analysis combined with gas phase chromatography and mass spectrometry (TGA-GC-MS). It is found that weakly adsorbed biphenyl produces a weight loss at temperatures below about 300°C; whereas, strongly adsorbed biphenyl produces a weight loss at temperatures from 300°C to as high as 1000°C. The amount of strongly adsorbed biphenyl is estimated by subtracting the amount of weakly adsorbed biphenyl from the total amount of biphenyl desorbed from the sample. A fully treated mordenite catalyst of this invention exhibits a sharp weight loss at temperatures below about 300°C, and little or no weight loss from 300°C to 1000°C. In contrast, acid-exchanged mordenite exhibits a sharp weight loss at temperatures below about 300°C, and a second weight loss starting at about 300°C and extending to 1000°C. It is believed that the weakly adsorbed biphenyl is located in sites from which there is relatively easy exit; whereas the strongly adsorbed biphenyl is located in sites from which there is relatively difficult exit. Thus, the acidic mordenite catalyst of this invention provides easy access and egress to adsorbed biphenyl. Such a theory, however, should not be construed to be binding or limiting of the scope of the invention.

The ratio of the aromatic compound to catalyst may be any weight ratio which produces alkylates enriched in the para-substituted isomers. Preferably, the weight ratio of aromatic compound to catalyst is in the range from 0.1:1 to 2000:1, more preferably from 10:1 to 500:1 and most preferably from 50:1 to 100:1. Below the preferred lower limit of 0.1:1, the yield of para-substituted products may be reduced. Above the preferred upper limit of 2000:1, the conversion of the polycyclic aromatic compound may be low.

The ratio of aromatic compound to alkylating agent may vary depending on the number of open para or beta positions on the aromatic compound. For example, if the aromatic compound to be alkylated has only one open para position, the ratio of alkylating agent to aromatic compound is 1:1. If the aromatic compound has two open para positions, the ratio is 2:1. The alkylating agent may be introduced to the reaction all at once, as in the case of a liquid alkylating reagent. Alternatively, the alkylating agent may be introduced to the reaction on demand until the desired degree of conversion is achieved, as in the case of a gaseous alkylating agent which is continuously fed into the reactor.

The contacting of the aromatic compound with the alkylating agent in the presence of the catalyst may occur in a reactor of any configuration. Batch-type and continuous reactors, such as fixed-bed, slurry bed, fluidized bed, catalytic distillation, or countercurrent reactors, are suitable configurations for the contact. Preferably, the reactor is fit with a means for observing and controlling the temperature of the reaction, a means for observing and measuring the pressure of the reaction, and optionally a means for agitating the reactants. The aromatic compound may be in the molten, liquid form or in solution. The alkylating agent may be introduced in the liquid or gaseous state, and may be added all at once at the start of the reaction, or fed continuously on demand from the reaction. The catalyst may be used in various forms, such as a fixed-bed, moving bed, fluidized bed, in suspension in the liquid reaction mixture, or in a reactive distillation column.

The contacting of the reactants in the presence of the catalyst may occur at any temperature or pressure which will produce as the major products the substituted aromatic compounds enriched in the para alkylated isomers. The temperature is in the range from 100°C to 400°C, preferably from 150°C to 300°C, more preferably from 175°C to 250°C. Below the lower limit of 100°C the reaction proceeds slowly. Above the upper limit of 400°C, the alkyl groups may scramble upsetting the selectivity for the para isomers. The pressure in the reactor is in the range from 10 to 500 psig (170 to 3549 kP), preferably from 30 to 300 psig (308 to 2170 kP), more preferably from 70 to 200 psig (584 to 1480 kP). Below the lower limit of 10 psig (170 kP) the catalyst begins to lose selectivity for para isomers. Above the upper limit of 500 psig (3549 kP) the preferred olefin alkylating agent will polymerize severely.

The aromatic compound, alkylating agent, and catalyst are contacted for a time sufficient to convert the aromatic compound to alkylated products, and sufficient to produce the desired yield of para-alkylated aromatic compounds. Generally, the contact time will depend on other reaction conditions, such as temperature, pressure and reagent/catalyst ratios. In a typical stirred batch reactor, for example, the reaction time is preferably in the range from 0.1 hour to 40 hours, more preferably from 0.5 to 20 hours.

The products of this invention include a mixture of alkylated aromatic compounds enriched in the para or linear alkylated isomers. The para or linear alkylated isomers are those in which the alkyl group(s) is(are) attached at the ends of the molecule, thereby yielding the product of smallest critical diameter. In the alkylation of biphenyl, for example, one such enriched product is the para,para'-dialkylate (4,4'-dialkylate). Likewise, in the alkylation of terphenyl, one such enriched product is the para',para"-dialkylate (4',4"-dialkylate). In the alkylation of naphthalene, a fused ring system, one such enriched product is the 2,6-dialkylate. Such products provide the smallest critical diameter to the alkylated molecule, and are also referred to as the "linear" alkylated products. All other alkylated products yield molecules of larger critical diameter.

For the purposes of this invention, the term "conversion" refers to the mole percent of aromatic compound which reacts to form alkylated products. Typically, in the batch reaction, the conversion achieved in the practice of this invention is at least about 20 mole percent, preferably about 50 mole percent, more preferably at least about 80 mole percent, and most preferably at least about 95 mole percent.

Likewise, the term "selectivity" refers to the mole percent of reacted polycyclic aromatic compound which is converted to a specific alkylated product. For example, in the practice of this invention biphenyl is converted to alkylates enriched in the p,p'-dialkylate, 4,4'-di(1-methylethyl)-1,1'-biphenyl. Smaller amounts of the 3- and 4-monoalkylated isomers, and the 3,4'-dialkylated isomer are obtained. Even smaller amounts of the 2-monoalkylated isomer and the dialkylates in which both alkyls are attached to one ring are obtained. Typically, the selectivity to total dialkylated biphenyls ranges from 25 to 80 mole percent. Typically, the selectivity to p,p'-dialkylated biphenyl achieved in the practice of this invention is at least about 20 mole percent, preferably at least about 40 mole percent, more preferably at least about 50 mole percent, most preferably at least about 70 mole percent. Typically, the selectivity to para or linear alkylates achieved in the practice of this invention is at least about 20 mole percent, preferably at least about 40 mole percent, more preferably about 50 mole percent, most preferably about 70 mole percent.

The selectivity for p,p'-dialkylates may also be expressed as the product $100 \times p,p'/\Sigma Di \times \Sigma Di/TA$. The first factor is the ratio $p,p'/\Sigma Di$, wherein p,p' represents the moles of p,p'-dialkylated isomer and ΣDi represents the total number of moles of dialkylated isomers. This ratio indicates the fraction of the total dialkylates which are the p,p' isomer. Typically, this ratio, expressed as a percentage, is at least about 40 mole percent, preferably at least about 60 mole percent, more preferably at least about 70 mole percent, most preferably greater than about 80 mole percent. The second factor is the ratio $\Sigma Di/TA$, wherein ΣDi is defined as above and TA is the total number of moles of all alkylated products. This ratio indicates the fraction of all alkylated products which are dialkylates. Typically, this ratio, expressed as a percentage, is at least about 15 mole percent, preferably at least about 30 mole percent, more preferably at least about 50 mole percent, most preferably at least about 70 mole percent.

The concept of simultaneous high conversion and high selectivity to the para alkylated aromatic compounds may be expressed conveniently in terms of yield. For the purposes of the present invention, the term "yield" refers to the numerical product of conversion and selectivity. For example, a process according to the present invention operating at a conversion of 0.982, or 98.2 percent, and a selectivity to para alkylated isomer of 0.650, or 65 percent, would have a 5 yield of the para isomer of 0.638, or 63.8 percent, which is the numerical product of 0.982 and 0.650. Typically, the yield of total dialkylates achieved in the process of this invention is at least 20 mole percent, preferably at least 55 mole percent, more preferably at least 75 mole percent. In contrast to the alkylations of the prior art, the process of the present 10 invention may be operated to give higher yields of the para alkylated isomers. Typical yields of the para alkylated isomers are at least about 10 mole percent, preferably at least about 40 mole percent, more preferably at least about 55 mole percent, most preferably at least about 70 mol percent.

Following the alkylation of the aromatic compound, the product mixture may be separated by standard techniques, such as distillation, melt crystallization, or solvent-assisted recrystallization. In the case of a product mixture containing biphenyl and its propylated derivatives, distillation is a convenient method of separating the products. Biphenyl may be removed in a first distillation column; 3-(1-methylethyl)-1,1'-biphenyl, 4-(1-methylethyl)-1,1'-biphenyl, and 3,4'-di(-methylethyl)-1,1'-biphenyl may be removed in a second distillation column. The bottoms may be transported to a third distillation column from which enriched 4,4'-di(1-methylethyl)-1,1'-biphenyl is distilled off. The final residuals contain small 15 amounts of triisopropylbiphenyls. 2-, 3-, and 4-Monoalkylates and residual dialkylates may be used as chemical intermediates, as high temperature heat-transfer fluids, or as solvents. Alternatively, these by-products and any triisopropylbiphenyls may be converted via transalkylation with benzene to valuable biphenyl and cumene. The p,p'-dialkylate 20 fraction may be upgraded to a purity greater than 99 weight percent by melt recrystallization.

Specific Embodiments

The following examples are given to illustrate the catalyst and the process of this invention and should not be construed as limiting its scope. All percentages in the examples are mole percent unless otherwise indicated. 25

Example 1 - Preparation of Acidic Mordenite Catalyst

A crystalline sodium mordenite is selected with the following properties: a SiO₂/Al₂O₃ ratio of 15, a SiO₂/Na₂O ratio 30 of 15, a crystallite size of 1000 Å with aggregates ranging in size from 1 to 20 microns, a Symmetry Index of 0.97 as determined by X-ray diffraction on a Philips Electronic spectrometer using the K α 1 line of copper; and a Langmuir surface area of 303 m²/g. The total pore volume of the sodium mordenite, determined on a Quantachrome Digidorb-6 unit using nitrogen as the adsorbate at 77K, is found to be 0.194 cc/g. The micropore volume, as determined by a t-plot, is found to be 0.046 cc/g. The transitional pore volume, given by the difference (0.194 cc/g - 0.046 cc/g), equals 0.148 cc/g, of which 0.083 cc/g are due to mesopores, and 0.065 cc/g are due to macropores. 35

The sodium mordenite (200 g), described hereinabove, is converted to acidic mordenite via exchange with 2000 ml of 1N aqueous hydrochloric acid at room temperature for thirty minutes. The mordenite-acid slurry is maintained homogeneous by agitation during this period, after which the acid-treated mordenite is isolated by filtration. The filtered solid is washed by suspension in 2000 ml of water, refiltered, and dried in air at 110°C. The dried solid is heated to 700°C in 40 flowing air for 2 hours. The heated solid is cooled to room temperature in air. The heat-treated acidic mordenite is mixed with 2000 ml of 6N nitric acid and maintained for 2 hours at refluxing temperature under vigorous stirring. After cooling to room temperature the solid is isolated by filtration and washed with water until free of residual acid. The washed solid is dried in air at 110°C to yield the acidic mordenite catalyst of the invention. Analysis of said catalyst by previously described methods gives the following results: a SiO₂:Al₂O₃ ratio of 256:1; a SiO₂:Na₂O ratio of 3732:1; a Symmetry 45 Index of 1.17; a Langmuir surface area of 673 m²/g, a total pore volume of 0.408 cc/g; a micropore volume of 0.208 cc/g; a mesopore volume of 0.068 cc/g; a macropore volume of 0.132 cc/g; and a ratio of combined meso- and macropore volume to total pore volume of 0.49. The catalyst is activated by heating in air at 700°C for 2 hours.

Example 2 - Alkylation of Biphenyl

A one-liter stirred tank reactor is equipped with a means for observing and controlling temperature, a means for observing and controlling pressure, and a means for agitating the contents of the reactor. Biphenyl (500 g) and the acidic mordenite catalyst of Example 1 (10 g) are added to the reactor. The reactor is sealed and purged with gaseous propylene. The reactor is pressurized with gaseous propylene to 120 psig, and then heated to 250°C. The reactor 50 contents are agitated at 2000 rpm. As propylene is consumed by the reaction, additional propylene is continuously fed to the reactor so as to maintain a total pressure of 120 psig. The reactor is sampled at 4 hours and 9 hours, and the products are analyzed by gas-phase chromatography. The results are set forth in Table I.

TABLE I

Example	Time (hr)	% Conversion	% p,p' Yield	% p,p'/ΣDi	% ΣDi/TA
2(a)	4	84	45	86	62
2(b)	9	98	60	86	71

"Di" represents dialkylated biphenyls. "ΣDi" is the sum of the moles of p,p', p,m' and m,m' dialkylates. "TA" represents total moles of alkylbiphenyls.

Example 3 -Alkylation of Diphenyl Ether

Diphenyl ether (500 g) and the catalyst of Example 1 (10 g) are contacted with propylene at a pressure of 100 psig (791 kP) and a temperature of 250°C for 20 hours. Analysis of the product mixture gives a conversion of 98.7 percent and a yield of p,p'-dialkylate of 63.4 percent. The p,p'/ΣDi factor is 82 percent, and the ΣDi/TA factor is 80 percent.

Example 4 -Alkylation of Naphthalene

Naphthalene (500 g) and the catalyst of Example 1 (10 g) are added to the reactor of Example 2. Propylene gas is added to the reactor to a total pressure of 120 psig (929 kP). The reactor is heated at 250°C for 20 hours, while maintaining the pressure at 120 psig (929 kP). Analysis of the products by gas chromatography gives a conversion of 97.3 percent, a yield of 2,6'-dialkylate of 42.7 percent, and a yield of 2,7'-dialkylate of 20 percent. The 2,6'/ΣDi factor is 64 percent, and the ΣDi/TA factor is 68 percent, wherein "ΣDi" represents the total moles of dialkylated naphthalenes and "TA" represents the total moles of alkylated products.

Example 5 -Alkylation of Diphenylmethane

Diphenylmethane (500 g) and the catalyst of Example 1 (10 g) are contacted with propylene at a temperature of 250°C and a pressure of 120 psig (929 kP) for 20 hours. Analysis of the product mixture gives a conversion of 98.5 percent, a yield of p,m'-dialkylate of 43.8 percent, and a yield of p,p'-dialkylate of 25.5 percent. The p,p'/ΣDi factor is 34 percent, and the ΣDi/TA factor is 77 percent.

Claims

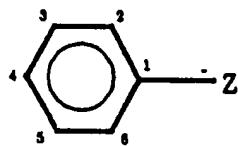
1. A process of alkylating an aromatic compound to a mixture of substituted aromatic compounds enriched in the para or linear alkylated isomers, comprising the steps of contacting the aromatic compound with an alkylating agent in the presence of a catalyst and at a temperature in the range from 100°C to 400°C and under a pressure in the range from 170kP to 3549kP (10 to 500psig), said catalyst comprising an acidic mordenite zeolite having a silica/alumina molar ratio of at least 50:1 and a crystalline structure which is determined by X-ray diffraction to possess a Symmetry Index of at least 1.0, said catalyst being prepared by a process which comprises:

(A) calcining in air or heating in an inert atmosphere an acidic mordenite zeolite having a Symmetry Index between 0.50 to 1.0 and a silica/alumina molar ratio less than 40:1, and thereafter
 (B) contacting the calcined or heated acidic mordenite zeolite with a strong acid to remove an amount of alumina sufficient to provide a silica/alumina ratio of at least 50:1, and optionally
 (C) repeating at least once the steps of (A) calcining or heating and (B) contacting with strong acid to remove additional alumina.

2. The process of Claim 1 wherein the aromatic compound is monocyclic.

3. The process of Claim 2 wherein the aromatic compound is represented by the formula:

5



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wherein Z is hydrogen, sulphydryl, alkyl of C₁-10 carbon atoms, aliphatic alkoxy or thioalkoxy of C₁-10 carbon atoms, fluoro, chloro, or bromo.

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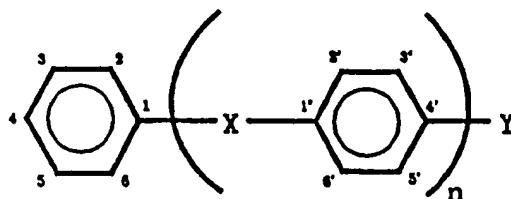
4. The process of Claim 3 wherein the aromatic compound is selected from the group consisting of benzene and cumene.

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5. The process of Claim 1, wherein the aromatic compound is a C₁₀-C₂₄ fused or non-fused polycyclic aromatic compound.

6. The process of Claim 5, wherein the non-fused polycyclic aromatic compound is represented by the formula:

25



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wherein n is a positive number from 1 to 3; Y is hydrogen, hydroxyl, sulphydryl, alkyl of C₁-10 carbon atoms, aliphatic alkoxy or thioalkoxy of C₁-10 carbon atoms, fluoro, chloro, or bromo; and X is absent or is O, S, SO, SO₂, CH₂, CH₂CH₂, CH₂CH₂CH₂ or CHCH₃.

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7. The process of Claim 6 wherein the polycyclic aromatic compound is biphenyl, naphthalene, or diphenyl ether.

8. The process of any one of the preceding claims wherein the alkylating agent is a monoolefin selected from propylene, n-butene, 1-hexene, cyclohexene, or 1-octene, a diolefin, or an alcohol.

9. The process of any one of the preceding claims, wherein the aromatic compound is in the neat, liquid state, and the alkylating agent is dissolved in the liquid state.

10. The process of any one of the preceding claims, wherein the aromatic compound is dissolved in a solvent selected from 1,3,5-triisopropyl-benzene or decalin.

45

11. The process of any one of the preceding claims, wherein the catalyst has a silica/alumina molar ratio of at least 50:1, a Symmetry Index of from 1.0 to 2.0, and a porosity such that the total pore volume is in the range from 0.18 cc/g to 0.45 cc/g and the ratio of the combined meso- and macropore volume to the total pore volume is in the range from 0.25 to 0.75.

50

12. The process of Claim 1, wherein the yield of the para alkylated isomers is at least 10 mole percent, and the yield of dialkylates is at least 20 mole percent.

13. The process of Claim 12 wherein the yield of para alkylated isomers is at least 70 mole percent.

55

14. A process of alkylating biphenyl to a mixture or disubstituted products enriched in 4,4'-dialkyl-1,1'-biphenyl, comprising the step of contacting biphenyl with an alkylating agent in the presence of a catalyst and at a temperature in the range from 100°C to 400°C and under a pressure in the range from 170kP to 3549kP (10 to 500psig) so that the 4,4'-dialkylated isomer is formed in a yield of at least 40 percent, said catalyst comprising an acidic mordenite

zeolite having a silica/alumina molar ratio of at least 50:1 and a crystalline structure which is determined by X-ray diffraction to possess a Symmetry Index of at least 1.0, said catalyst being prepared by a process which comprises:

5 (A) calcining in air or heating in an inert atmosphere an acidic mordenite zeolite having a Symmetry Index between 0.50 to 1.0 and a silica/alumina molar ratio less than 40:1, and thereafter
 (B) contacting the calcined or heated acidic mordenite zeolite with a strong acid to remove an amount of alumina sufficient to provide a silica/alumina ratio of at least 50:1, and optionally
 (C) repeating at least once the steps of (A) calcining or heating and (B) contacting with strong acid to remove additional alumina.

10 15. A process of alkylating benzene to a mixture of disubstituted products enriched in p-dialkylated benzene, comprising the step of contacting benzene with an alkylating agent in the presence of a catalyst and at a temperature in the range from 100°C to 400°C and under a pressure in the range from 170kP to 3549kP (10 to 500psig), said catalyst comprising an acidic mordenite zeolite having a silica/alumina molar ratio of at least 50:1 and a crystalline structure which is determined by X-ray diffraction to possess a Symmetry Index of at least 1.0, said catalyst being prepared by a process which comprises:

15 (A) calcining in air or heating in an inert atmosphere an acidic mordenite zeolite having a Symmetry Index between 0.50 to 1.0 and a silica/alumina molar ratio less than 40:1, and thereafter
 20 (B) contacting the calcined or heated acidic mordenite zeolite with a strong acid to remove an amount of alumina sufficient to provide a silica/alumina ratio of at least 50:1, and optionally
 (C) repeating at least once the steps of (A) calcining or heating and (B) contacting with strong acid to remove additional alumina.

25 16. The process of any of the preceding Claims wherein the mordenite zeolite used to prepare the catalyst has a Symmetry Index between 0.60 and 1.0 and is treated with an acid in a concentration ranging from 0.5 N to 3.0 N prior to the calcining or heating step (A).

30 17. The process of any of the preceding Claims wherein step (A) comprises calcination of the acidic mordenite zeolite in air, or heating it in an inert atmosphere, at a temperature between 250°C and 950°C.

35 18. The process of any of the preceding Claims wherein step (B) comprises contacting the calcined or heated mordenite zeolite from step (A) with a strong inorganic acid having a concentration in the range from 4 N to 12 N at a temperature in the range from 22°C to 220°C.

40 19. A catalyst composition comprising an acidic mordenite zeolite having a silica/alumina molar ratio of at least 50:1, a Symmetry Index of at least about 1, and a porosity such that the total pore volume is in the range of from 0.18cm³/g to 0.45cm³/g, and the ratio of the combined meso- and macropore volume to the total pore volume is from 0.25 to 0.75, said catalyst being prepared by a process which comprises:

45 (A) calcining in air or heating in an inert atmosphere an acidic mordenite zeolite having a Symmetry Index between 0.50 to 1.0 and a silica/alumina molar ratio less than 40:1, and thereafter
 (B) contacting the calcined or heated acidic mordenite zeolite with a strong acid to remove an amount of alumina sufficient to provide a silica/alumina ratio of at least 50:1, and optionally
 (C) repeating at least once the steps of (A) calcining or heating and (B) contacting with strong acid to remove additional alumina.

50 20. The catalyst composition as claimed in Claim 19 wherein the silica/alumina molar ratio is from 150:1 to 1000:1, and the Symmetry Index is in the range from 1.0 to 2.0.

55 21. The catalyst composition of Claim 19 or 20 wherein the crystalline structure of the starting mordenite zeolite comprises a matrix of Cmcm symmetry having dispersed therein domains with Cmmm symmetry.

22. The catalyst composition of any of Claims 19 to 21 wherein the mordenite zeolite catalyst is composited with a binder.

23. A process of preparing the catalyst composition of Claim 19 comprising the steps of (A) first calcining or heating and then (B) contacting with a strong acid an acidic mordenite zeolite having a silica/alumina molar ratio of less

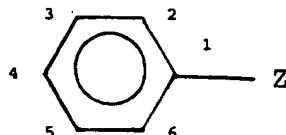
than 40:1 and a crystalline structure determined by X-ray diffraction to possess a Symmetry Index of from 0.5 to 1.0 under conditions sufficient to remove an amount of alumina to provide a silica/alumina ratio of at least 50:1.

Patentansprüche

5 1. Verfahren zum Alkylieren einer aromatischen Verbindung zu einem Gemisch von substituierten aromatischen Verbindungen, das angereichert ist an para- oder linear alkylierten Isomeren, wobei das Verfahren die Stufen umfaßt, in denen man die aromatische Verbindung in Gegenwart eines Katalysators und bei einer Temperatur im Bereich von 100°C bis 400°C sowie unter einem Druck im Bereich von 170kP bis 3.549kP (10 bis 500psig) mit einem Alkylierungsmittel in Berührung bringt, wobei der Katalysator einen sauren Mordenit-Zeolith mit einem Siliciumdioxid/Aluminiumoxid-Molverhältnis von mindestens 50:1 und mit einer Kristallstruktur enthält, die nach Röntgenstrahlbeugungsanalyse einen Symmetriewert von mindestens 1,0 aufweist, und wobei der Katalysator nach einem Verfahren hergestellt wurde, bei dem man:

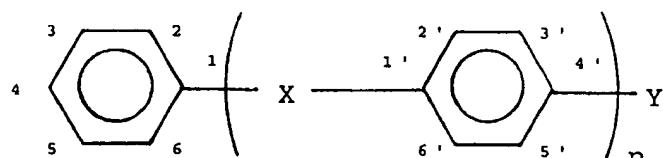
15 (A) einen sauren Mordenit-Zeolith mit einem Symmetriewert zwischen 0,50 und 1,0 und einem Siliciumdioxid/Aluminiumoxid-Molverhältnis von kleiner als 40:1 in Luft kalziniert oder in einer inerten Atmosphäre erhitzt und danach
 (B) den kalzinierten oder erhitzten sauren Mordenit-Zeolith mit einer starken Säure in Berührung bringt, um eine genügende Menge Aluminiumoxid zu entfernen, so daß das Siliciumdioxid/Aluminiumoxid-Verhältnis mindestens 50:1 beträgt, und gegebenenfalls
 20 (C) den Katalysator mindestens ein weiteres Mal gemäß der Stufe (A) kalziniert oder erhitzt und gemäß der Stufe (B) mit starker Säure in Berührung bringt, um weiteres Aluminiumoxid zu entfernen.

25 2. Verfahren nach Anspruch 1, wobei die aromatische Verbindung monocyclisch ist.
 3. Verfahren nach Anspruch 2, wobei die aromatische Verbindung durch die Formel



35 wiedergegeben wird, in der Z für Wasserstoff, Sulfhydryl, Alkyl mit 1 bis 10 Kohlenstoffatomen, einen aliphatischen Alkoxy- oder Thioalkoxyrest mit 1 bis 10 Kohlenstoffatomen, Fluor, Chlor oder Brom steht.

40 4. Verfahren nach Anspruch 3, wobei die aromatische Verbindung ausgewählt ist aus der Gruppe, die aus Benzol und Cumol besteht.
 5. Verfahren nach Anspruch 1, wobei die aromatische Verbindung eine kondensierte oder nichtkondensierte polycyclische aromatische Verbindung mit 10 bis 24 Kohlenstoffatomen ist.
 45 6. Verfahren nach Anspruch 5, wobei die nichtkondensierte polycyclische aromatische Verbindung durch die Formel



55 wiedergegeben wird, in der n eine positive Zahl von 1 bis 3 bedeutet; Y für Wasserstoff, Hydroxyl, Sulfhydryl, Alkyl mit 1 bis 10 Kohlenstoffatomen, einen aliphatischen Alkoxy- oder Thioalkoxyrest mit 1 bis 10 Kohlenstoffatomen, Fluor, Chlor oder Brom steht und X entweder fehlt oder für O, S, SO, SO2, CH2, CH2CH2, CH2CH2CH2 oder CHCH3 steht.

7. Verfahren nach Anspruch 6, wobei die polycyclische aromatische Verbindung Biphenyl, Naphthalin oder Diphenylether ist.
8. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Alkylierungsmittel ein Monoolefin, das aus Propylen, n-Buten, 1-Hexen, Cyclohexen oder 1-Octen ausgewählt wurde, oder ein Diolefin oder ein Alkohol ist.
9. Verfahren nach einem der vorhergehenden Ansprüche, wobei die aromatische Verbindung in unverdünntem, flüssigem Zustand vorliegt und das Alkylierungsmittel darin gelöst ist.
10. Verfahren nach einem der vorhergehenden Ansprüche, wobei die aromatische Verbindung in einem Lösungsmittel gelöst ist, das aus 1,3,5-Triisopropylbenzol oder Dekalin ausgewählt wurde.
11. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Katalysator ein Siliciumdioxid/Aluminiumoxid-Molverhältnis von mindestens 50:1, einen Symmetrieindex von 1,0 bis 2,0 und eine solche Porosität hat, daß das gesamte Porenvolumen im Bereich von 0,18 cm³/g bis 0,45 cm³/g und das Verhältnis des Volumens der vereinigten Meso- und Makroporen zu dem gesamten Porenvolumen im Bereich von 0,25 bis 0,75 liegt.
12. Verfahren nach Anspruch 1, wobei die Ausbeute an para-alkylierten Isomeren mindestens 10 Molprozent und die Ausbeute an Dialkylaten mindestens 20 Molprozent beträgt.
13. Verfahren nach Anspruch 12, wobei die Ausbeute an para-alkylierten Isomeren mindestens 70 Molprozent beträgt.
14. Verfahren zum Alkylieren von Biphenyl zu einem Gemisch von disubstituierten Produkten, das an 4,4'-Dia1kyl-1,1'-biphenyl angereichert ist, wobei das Verfahren die Stufe umfaßt, in der man Biphenyl in Gegenwart eines Katalysators und bei einer Temperatur im Bereich von 100°C bis 400°C sowie unter einem Druck im Bereich von 170kP bis 3.549kP (10 bis 500psig) mit einem Alkylierungsmittel in Berührung bringt, so daß das 4,4'-dialkylierte Isomere in einer Ausbeute von mindestens 40 Prozent gebildet wird, wobei der Katalysator einen sauren Mordenit-Zeolith mit einem Siliciumdioxid/Aluminiumoxid-Molverhältnis von mindestens 50:1 und mit einer Kristallstruktur enthält, die nach Röntgenstrahlbeugungsanalyse einen Symmetrieindex von mindestens 1,0 aufweist, und wobei der Katalysator nach einem Verfahren hergestellt wurde, bei dem man:
 - (A) einen sauren Mordenit-Zeolith mit einem Symmetrieindex zwischen 0,50 und 1,0 und einem Siliciumdioxid/Aluminiumoxid-Molverhältnis von kleiner als 40:1 in Luft kalziniert oder in einer inerten Atmosphäre erhitzt und danach
 - (B) den kalzinierten oder erhitzten sauren Mordenit-Zeolith mit einer starken Säure in Berührung bringt, um eine genügende Menge Aluminiumoxid zu entfernen, so daß das Siliciumdioxid/Aluminiumoxid-Verhältnis mindestens 50:1 beträgt, und gegebenenfalls
 - (C) den Katalysator mindestens ein weiteres Mal gemäß der Stufe (A) kalziniert oder erhitzt und gemäß der Stufe (B) mit starker Säure in Berührung bringt, um weiteres Aluminiumoxid zu entfernen.
15. Verfahren zum Alkylieren von Benzol zu einem Gemisch von disubstituierten Produkten, das an para-dialkylierten Benzolen angereichert ist, wobei das Verfahren die Stufe umfaßt, in der man Benzol in Gegenwart eines Katalysators und bei einer Temperatur im Bereich von 100°C bis 400°C sowie unter einem Druck im Bereich von 170kP bis 3.549kP (10 bis 500psig) mit einem Alkylierungsmittel in Berührung bringt, wobei der Katalysator einen sauren Mordenit-Zeolith mit einem Siliciumdioxid/Aluminiumoxid-Molverhältnis von mindestens 50:1 und mit einer Kristallstruktur enthält, die nach Röntgenstrahlbeugungsanalyse einen Symmetrieindex von mindestens 1,0 aufweist, und wobei der Katalysator nach einem Verfahren hergestellt wurde, bei dem man:
 - (A) einen sauren Mordenit-Zeolith mit einem Symmetrieindex zwischen 0,50 und 1,0 und einem Siliciumdioxid/Aluminiumoxid-Molverhältnis von kleiner als 40:1 in Luft kalziniert oder in einer inerten Atmosphäre erhitzt und danach
 - (B) den kalzinierten oder erhitzten sauren Mordenit-Zeolith mit einer starken Säure in Berührung bringt, um eine genügende Menge Aluminiumoxid zu entfernen, so daß das Siliciumdioxid/Aluminiumoxid-Verhältnis mindestens 50:1 beträgt, und gegebenenfalls
 - (C) den Katalysator mindestens ein weiteres Mal gemäß der Stufe (A) kalziniert oder erhitzt und gemäß der Stufe (B) mit starker Säure in Berührung bringt, um weiteres Aluminiumoxid zu entfernen.

16. Verfahren nach einem der vorhergehenden Ansprüche, wobei der für die Herstellung des Katalysators verwendete Mordenit-Zeolith einen Symmetrieindex zwischen 0,60 und 1,0 hat und vor dem Kalzinieren oder Erhitzen gemäß der Stufe (A) mit einer Säure in einer Konzentration von 0,5n bis 3,0n behandelt wird.

5 17. Verfahren nach einem der vorhergehenden Ansprüche, wobei man in der Stufe (A) den sauren Mordenit-Zeolith bei einer Temperatur zwischen 250°C und 950°C in Luft kalziniert oder in einer inerten Atmosphäre erhitzt.

10 18. Verfahren nach einem der vorhergehenden Ansprüche, wobei man in der Stufe (B) den in der Stufe (A) kalzinierten oder erhitzten Mordenit-Zeolith mit einer starken anorganischen Säure in einer Konzentration im Bereich von 4n bis 12n bei einer Temperatur im Bereich von 22°C bis 220°C behandelt.

15 19. Katalysator, enthaltend einen sauren Mordenit-Zeolith mit einem Siliciumdioxid/Aluminiumoxid-Molverhältnis von mindestens 50:1, einen Symmetrieindex von mindestens etwa 1 und einer solchen Porösität, daß das gesamte Porenvolumen im Bereich von 0,18 cm³/g bis 0,45 cm³/g liegt und das Verhältnis des Volumens der vereinigten Meso- und Makroporen zu dem gesamten Porenvolumen 0,25 bis 0,75 beträgt, wobei der Katalysator nach einem Verfahren hergestellt wurde, bei dem man:

20 (A) einen sauren Mordenit-Zeolith mit einem Symmetrieindex zwischen 0,50 und 1,0 und einem Siliciumdioxid/Aluminiumoxid-Molverhältnis von kleiner als 40:1 in Luft kalziniert oder in einer inerten Atmosphäre erhitzt und danach

25 (B) den kalzinierten oder erhitzten sauren Mordenit-Zeolith mit einer starken Säure in Berührung bringt, um eine genügende Menge Aluminiumoxid zu entfernen, so daß das Siliciumdioxid/Aluminiumoxid-Verhältnis mindestens 50:1 beträgt, und gegebenenfalls

(C) den Katalysator mindestens ein weiteres Mal gemäß der Stufe (A) kalziniert oder erhitzt und gemäß der Stufe (B) mit starker Säure in Berührung bringt, um weiteres Aluminiumoxid zu entfernen.

20 20. Katalysator nach Anspruch 19, wobei das Siliciumdioxid/Aluminiumoxid-Molverhältnis von 150:1 bis 1.000:1 beträgt und der Symmetrieindex im Bereich von 1,0 bis 2,0 liegt.

30 21. Katalysator nach Anspruch 19 oder 20, wobei die Kristallstruktur des als Ausgangsstoff verwendeten Mordenit-Zeoliths eine Matrix mit Cmcm-Symmetrie enthält, in der Domänen mit Cmmm-Symmetrie dispergiert sind.

35 22. Katalysator nach einem der Ansprüche 19 bis 21, wobei der Mordenit-Zeolith-Katalysator mit einem Bindemittel verbunden ist.

40 23. Verfahren zur Herstellung des Katalysators nach Anspruch 19, welches die Stufen umfaßt, in denen man einen sauren Mordenit-Zeolith mit einem Siliciumdioxid/Aluminiumoxid-Molverhältnis von kleiner als 40:1 und einer durch Röntgenbeugungsanalyse bestimmten Kristallstruktur mit einem Symmetrieindex von 0,5 bis 1,0 (A) zuerst kalziniert oder erhitzt und dann (B) mit einer starken Säure in Berührung bringt, unter Bedingungen, die ausreichen, um eine solche Menge Aluminiumoxid zu entfernen, daß das Siliciumdioxid/Aluminiumoxid-Verhältnis mindestens 50:1 beträgt.

Revendications

45 1. Procédé d'alkylation d'un composé aromatique en un mélange de composés aromatiques substitués enrichi en isomères para- ou linéaires alkylés, comprenant les étapes consistant à mettre en contact le composé aromatique avec un agent d'alkylation en présence d'un catalyseur, à une température comprise entre 100°C et 400°C et sous une pression comprise entre 170 kP et 3 549 kP (10 et 500 psig), ledit catalyseur comprenant une zéolite de mordénite acide ayant un rapport molaire silice/alumine d'au moins 50:1 et une structure cristalline, qui est déterminée par diffraction des rayons X, ayant un indice de symétrie d'au moins 1,0, ledit catalyseur étant préparé à l'aide d'un procédé qui consiste:

50 (A) à calciner dans l'air ou à chauffer dans une atmosphère inerte une zéolite de mordénite acide ayant un indice de symétrie compris entre 0,50 et 1,0 et un rapport molaire silice/alumine inférieur à 40:1, et ensuite

55 (B) à mettre en contact la zéolite de mordénite acide calcinée ou chauffée avec un acide fort afin d'éliminer une quantité d'alumine suffisante pour fournir un rapport silice/alumine d'au moins 50:1, et, éventuellement,

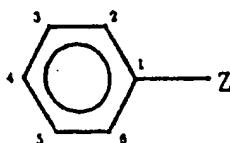
(C) à répéter au moins une fois les étapes (A) de calcination ou de chauffage et (B) de mise en contact avec un acide fort pour éliminer une quantité supplémentaire d'alumine.

2. Procédé selon la revendication 1, dans lequel le composé aromatique est monocyclique.

3. Procédé selon la revendication 2, dans lequel le composé aromatique est représenté par la formule

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dans laquelle Z est un atome d'hydrogène, un groupe sulfhydryle, alkyle ayant de 1 à 10 atomes de carbone, alcoxy ou thioalcoxy aliphatique ayant de 1 à 10 atomes de carbone, fluoro, chloro ou bromo.

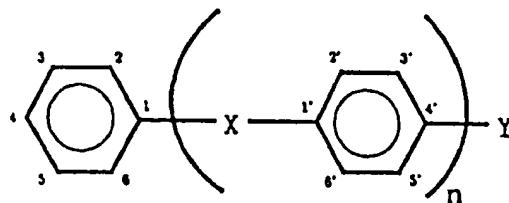
15 4. Procédé selon la revendication 3, dans lequel le composé aromatique est choisi dans le groupe formé par le benzène et le cumène.

5. Procédé selon la revendication 1, dans lequel le composé aromatique est un composé aromatique polycyclique en C₁₀ à C₂₄ condensé ou non-condensé.

20 6. Procédé selon la revendication 5, dans lequel le composé aromatique polycyclique non condensé est représenté par la formule:

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dans laquelle n est un nombre entier positif de 1 à 3; Y est un atome d'hydrogène, un groupe hydroxyle, sulfhydryle, alkyle ayant de 1 à 10 atomes de carbone, alcoxy ou thioalcoxy aliphatique ayant de 1 à 10 atomes de carbone, fluoro, chloro, ou bromo; et X est absent ou est O, S, SO, SO₂, CH₂, CH₂CH₂, CH₂CH₂CH₂ ou CHCH₃.

35 7. Procédé selon la revendication 6, dans lequel le composé aromatique polycyclique est le biphenyle, le naphtalène ou l'éther diphénylique.

40 8. Procédé selon l'une des revendications précédentes, dans lequel l'agent d'alkylation est une monooléfine choisie parmi le propylène, le n-butène, le 1-hexène, le cyclohexène, ou le 1-octène, une dioléfine ou un alcool.

9. Procédé selon l'une des revendications précédentes, dans lequel le composé aromatique est à l'état pur, liquide, et l'agent d'alkylation est dissous à l'état liquide.

45 10. Procédé selon l'une des revendications précédentes, dans lequel le composé aromatique est dissous dans un solvant choisi parmi le 1,3,5-triisopropyl-benzène ou la décaline.

50 11. Procédé selon l'une des revendications précédentes, dans lequel le catalyseur a un rapport molaire silice/alumine d'au moins 50:1, un indice de symétrie compris entre 1,0 et 2,0, et une porosité telle que le volume total de pores est compris entre 0,18 cm³/g et 0,45 cm³/g et le rapport du volume combiné de méso- et macropores au volume total de pores est compris entre 0,25 et 0,75.

55 12. Procédé selon la revendication 1, dans lequel le rendement des isomères para-alkylés est au moins 10 pour-cent en moles, et le rendement des dialkylates est au moins 20 pour-cent en moles.

13. Procédé selon la revendication 12, dans lequel le rendement des isomères para-alkylés est d'au moins 70 pour-cent en moles.

14. Procédé d'alkylation du biphenyle en un mélange de produits disubstitués enrichi en 4,4'-dialkyl-1,1'-biphenyle, comprenant l'étape consistant à mettre en contact le biphenyle avec un agent d'alkylation en présence d'un catalyseur et à une température comprise entre 100°C et 400°C et à une pression comprise entre 170 kPa et 3 549 kPa (10 et 500 psig) de sorte de l'isomère 4,4'-dialkylé se forme avec un rendement d'au moins 40 pour-cent, ledit catalyseur comprenant une zéolite de mordénite acide ayant un rapport molaire silice/alumine d'au moins 50:1 et une structure cristalline, qui est déterminée par une diffraction des rayons X, comme ayant un indice de symétrie d'au moins 1,0, ledit catalyseur étant préparé à l'aide d'un procédé qui consiste:

10 (A) à calciner dans l'air ou à chauffer dans une atmosphère inerte une zéolite de mordénite acide ayant un indice de symétrie compris entre 0,50 et 1,0 et un rapport molaire silice/alumine inférieur à 40:1, et ensuite (B) à mettre en contact la zéolite de mordénite acide calcinée ou chauffée avec un acide fort afin d'éliminer une quantité d'alumine suffisante pour fournir un rapport silice/alumine d'au moins 50:1, et, éventuellement, (C) à répéter au moins une fois les étapes (A) de calcination ou de chauffage et (B) de mise en contact avec un acide fort pour éliminer une quantité supplémentaire d'alumine.

15 15. Procédé d'alkylation du benzène en un mélange de produits disubstitués enrichi en benzène p-dialkylé, comprenant l'étape de mise en contact du benzène avec un agent d'alkylation en présence d'un catalyseur, à une température comprise entre 100°C et 400°C et sous une pression comprise entre 170 kPa et 3 549 kPa (10 et 500 psig), ledit catalyseur comprenant une zéolite de mordénite acide ayant un rapport molaire silice/alumine d'au moins 50:1 et une structure cristalline, qui est déterminée par diffraction des rayons X, comme ayant un indice de symétrie d'au moins 1,0, ledit catalyseur étant préparé à l'aide d'un procédé qui consiste:

20 (A) à calciner dans l'air ou à chauffer dans une atmosphère inerte une zéolite de mordénite acide ayant un indice de symétrie compris entre 0,50 et 1,0 et un rapport molaire silice/alumine inférieur à 40:1, et ensuite (B) à mettre en contact la zéolite de mordénite acide calcinée ou chauffée avec un acide fort afin d'éliminer une quantité d'alumine suffisante pour fournir un rapport silice/alumine d'au moins 50:1, et, éventuellement, (C) à répéter au moins une fois les étapes (A) de calcination ou de chauffage et (B) de mise en contact avec un acide fort pour éliminer une quantité supplémentaire d'alumine.

30 16. Procédé selon l'une des revendications précédentes, dans lequel la zéolite de mordénite utilisée pour préparer le catalyseur possède un indice de symétrie compris entre 0,60 et 1,0 et est traitée par un acide en une concentration comprise 0,5 N et 3,0 N avant l'étape de calcination ou de chauffage (A).

35 17. Procédé selon l'une des revendications précédentes, dans lequel l'étape (A) comprend la calcination de la zéolite de mordénite acide dans l'air, ou son chauffage dans une atmosphère inerte, à une température comprise entre 250°C et 950°C.

40 18. Procédé selon l'une des revendications précédentes, dans lequel l'étape (B) comprend la mise en contact de la zéolite de mordénite calcinée ou chauffée de l'étape (A) avec un acide minéral fort ayant une concentration comprise entre 4 N et 12 N à une température comprise entre 22°C et 220°C.

45 19. Composition catalytique comprenant une zéolite de mordénite acide ayant un rapport molaire silice/alumine d'au moins 50:1, un indice de symétrie d'au moins environ 1, et une porosité telle que le volume total de pores soit compris entre 0,18 cm³/g et 0,45 cm³/g, et que le rapport du volume combiné de méso- et macropores au volume total de pores soit compris entre 0,25 et 0,75, ledit catalyseur étant préparé à l'aide d'un procédé qui consiste:

50 (A) à calciner dans l'air ou à chauffer dans une atmosphère inerte une zéolite de mordénite acide ayant un indice de symétrie compris entre 0,50 et 1,0 et un rapport molaire silice/alumine inférieur à 40:1, et ensuite (B) à mettre en contact la zéolite de mordénite acide calcinée ou chauffée avec un acide fort afin d'éliminer une quantité d'alumine suffisante pour fournir un rapport silice/alumine d'au moins 50:1, et, éventuellement, (C) à répéter au moins une fois les étapes (A) de calcination ou de chauffage et (B) de mise en contact avec un acide fort pour éliminer une quantité supplémentaire d'alumine.

55 20. Composition catalytique selon la revendication 19, dans laquelle le rapport molaire silice/alumine est compris entre 150:1 et 1 000:1, et l'indice de symétrie est compris entre 1,0 et 2,0.

21. Composition catalytique selon la revendication 19 ou 20, dans laquelle la structure cristalline de la zéolite de mordénite de départ comprend un matrice de symétrie CmCm contenant sous forme dispersée des domaines avec une symétrie Cmmm.

22. Composition catalytique selon l'une des revendications 19 à 21, dans laquelle le catalyseur de zéolite de mordénite est formulé avec un liant.

5 23. Procédé de préparation de la composition catalytique selon la revendication 19 comprenant les étapes consistant (A) d'abord à calciner ou à chauffer et (B) ensuite à mettre en contact avec un acide fort une zéolite de mordénite acide ayant un rapport molaire silice/alumine inférieur à 40:1 et une structure cristalline, telle que déterminée par diffraction des rayons X, ayant un indice de symétrie compris entre 0,5 et 1,0 dans des conditions suffisantes pour éliminer une quantité d'alumine afin d'obtenir un rapport silice/alumine d'au moins 50:1.

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